Origin of negative differential resistance in a strongly coupled single molecule-metal junction device

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A new mechanism is proposed to explain the origin of negative differential resistance (NDR) in a strongly coupled single molecule-metal junction. A first-principles quantum transport calculation in a Fe-terpyridine linker molecule sandwiched between a pair of gold electrodes is presented. Upon increasing applied bias, it is found that a new *phase* in the broken symmetry wavefunction of the molecule emerges from the mixing of occupied and unoccupied molecular orbital. As a consequence, a non-linear change in the coupling between molecule and lead is evolved resulting to NDR. This model can be used to explain NDR in other class of metal-molecule junction device.

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The controlled transport of electrons in metal-molecule junction has been an active field of research for the last decade [1], with an aim to find a possible solution to the miniaturization impasse that semiconductor industry is facing currently. Researchers have already demonstrated conduction, rectification, and switching in metal-molecule junction devices [2, 3, 4]. Among all, the demonstration of a single-molecule switch with a NDR feature [2] has drawn considerable attention in recent years. The NDR feature is described by a steady increase followed by a decrease in current (I) with the increase in applied bias (V). Since its realization [2], various groups have been working on this problem to unravel the *true* mechanism of NDR in molecular junction, understanding of which would revolutionize the field of molecular electronics [1]. Different mechanisms have been proposed to explain the observed NDR [2, 5, 6, 7] in metal-molecule junctions. For example, in *weakly coupled* junction, it is argued [5, 8, 9] that the narrow density of states (DOS) feature of the tip apex atom is responsible for the NDR. But in contrast, very recently, it is proposed [6] that the local orbital symmetry matching between the tip and the molecule is the cause of the observed NDR. In another example [2], the bias induced charging and conformational change of the molecule is suggested as the viable mechanism for inducing NDR. However, it should be noted that controversies still remain regarding whether the conformational change arising from the rotaion of the ligand group [10] or from the rotation of the molecular group [11, 12, 13] within the molecular backbone is responsible for the observed NDR. Another possible model for NDR based on polaron formation was also proposed very recently [14]. Based on a simple mean-field theory it is suggested [14] that NDR effect can be possible if the bias induced polaron formation would shift the energy level away from the window between the chemical potentials of the leads.

It can be seen from the above review that none of the proposed mechanisms thus far have stressed the importance of bias induced coupling change between molecule and lead. Bias induced relaxation of the molecular eigenstates will affect the coupling between molecule and lead, which would have a measurable effect in altering the $I - V$ feature. Furthermore, it is still controversial whether the NDR is intrinsic to the molecule or junction dependent. Here, we propose a *new consistent and unified model* to explain the origin of NDR in a strongly coupled metal-molecule junction. It is found that a new *phase* in the broken symmetry wavefunction of the molecule arising from the mixing of occupied and unoccipied molecular orbital upon increasing applied bias leading to a non-linear change in the coupling between molecule and lead is responsible for the observed NDR. Our calculation further reveals, even if we have a symmetric molecule-lead junction at zero bias, the asymmetric channel coupling at the junction upon applied bias originating from the phase reversal of the molecular eigenstate can produce asymmetric I-V characteristic.
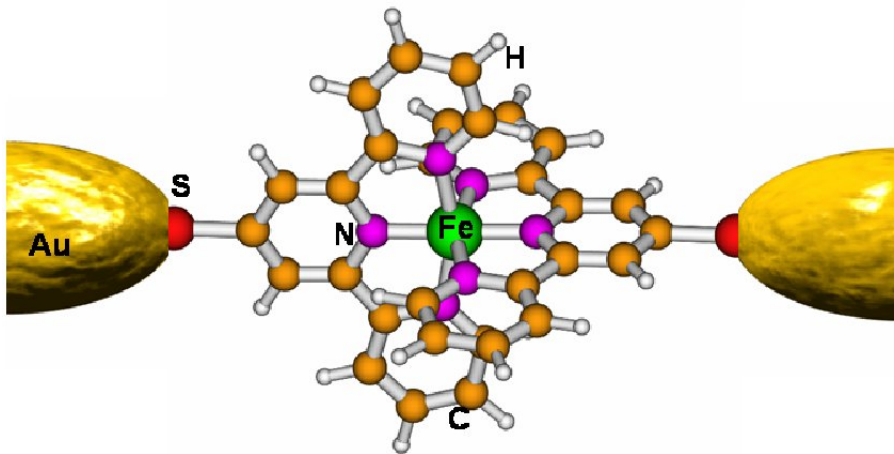
FIG. 1: (color online) Schematic of the strongly coupled single molecule (FETP)-gold junction.

We have used a self-consistent *many body* approach to investigate the quantum transport properties of a Fe-terpyridine linker molecule (FETP) sandwiched between two gold electrodes (Fig. 1). The choice behind the selection of FETP molecule is prompted by the recent interest in organo metallic molecule [15] in molecular electronics. Furthermore, very recently it has been shown organo-metallic molecule exhibiting NDR behavior [5]. The electric field effect for each applied bias [16] is explicitly included in our calculation within a *many body* framework. The non equilibrium Green's function (NEGF) approach is used to calculate the quantum transport. Our calculation reveals strong-field induced asymmetry and NDR features with peak (I_p) to valley (I_v) current ratio (PVR) of 2.7 at both positive and negative bias. Even though the magnitude of calculated current differs between the positive and negative bias range, the $\frac{I_p}{I_v}$ remains about the same for both positive and negative bias.

In our calculation, we have used a real space approach in which the *many body* wavefunction is expanded in terms of finite set of atomic Gaussian orbital [17]. This allows us to partition the *open* molecular device structure into two regions of interest. The first is the *true* device region, which includes optimized FETP sandwiched between two 3 atoms gold clusters taken from Au (111) surface with the terminal S-atom at the three fold hollow fcc site[18] of the gold with S-Au distance 2.45 $\mathring{A}$. The second part is essentially the semi-infinite contact region, which is essentially assumed to be unperturbed by the molecular adsorption. As exact exchange with dynamical correlation plays a key role in determining accurate energy spectra in density functional theory, and consequently the $I - V$ feature, we have used a *posteriori* Becke's three parameter hybrid density functional approach (B3LYP) [17, 19] for our calculation. Los Alamos double zeta effective core potential basis set (LANL2DZ) [17], which includes the scalar relativistic effect,
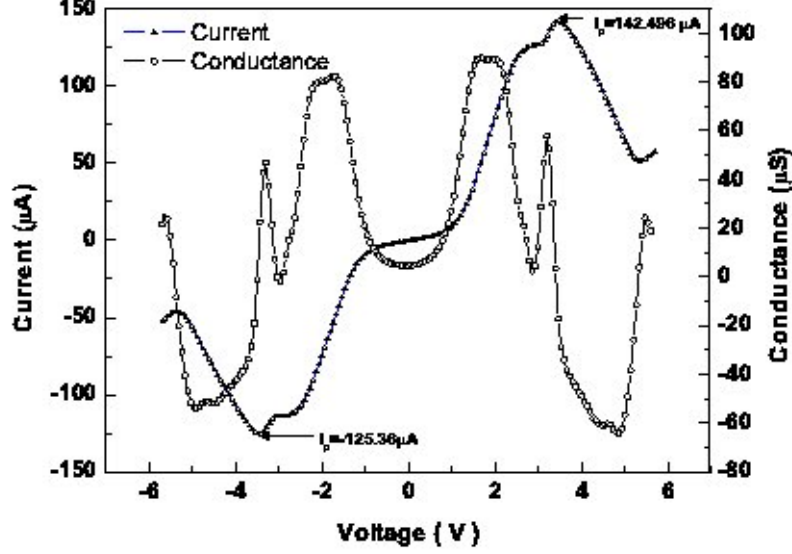
FIG. 2: Calculated current and conductance as a function of applied bias. I_p refers to the peak value for current.

is used for the calculation of the non equilibrium electronic structure. The non equilibrium Hamiltonian, $H(\varepsilon)$ of the true device region is calculated as [20], $H(\varepsilon) = H(0) + \vec{\varepsilon}.\sum_i \vec{r}(i)$, where $H(0)$ is the equilibrium *many body* Hamiltonian; $\vec{\varepsilon}$ is the applied dipole electric field, and $\vec{r}(i)$ is the coordinate of the electron i. This approach allows us to explicitly obtain the *true* non-equilibrium energy spectra including Stark shift. It should be noted that the convergence thresholds for energy, maximum and root mean square electron density are set at 10^{-6} a. u., 10^{-6} a. u. and 10^{-8} a. u. respectively to ensure *tight convergence* during self-consistent calculation. Subsequently, we constructed the NEGF G as: $G(\varepsilon) = (E \times I - H_{Mol}(\varepsilon) - \Sigma_l(\varepsilon) - \Sigma_r(\varepsilon))^{-1}$, where $H_{Mol}(\varepsilon)$ is the orthogonalized field dependent Kohn-Sham (KS) molecular Hamiltonian matrix obtained by suitable partitioning of $H(\varepsilon)$; E is the injection energy of the tunneling electron; I is the identity matrix. $\Sigma_{l,r}(\varepsilon)$ are the self-energy functions [21, 22] calculated from the *bias dependent* coupling matrices and the Green's function of the Au lead. The latter is approximated from the 6s-band density of states at the Fermi energy of bulk Au [23] and kept fixed for all bias points. The current in the molecular junction is calculated as [14, 15]: $I = \frac{2e}{h} \int_{\mu_1}^{\mu_2} T(E, V) \times [f(E, \mu_2) - f(E, \mu_1)] \times dE$, where $\mu_{1,2} = E_f \mp eV/2$; E_f is the equilibrium Fermi energy (-4.69 eV). f is the fermi distribution function. $T(E, V)$ is the bias dependent transmission function [15] obtained from non-equilibrium G and Σs.

First we comment on our calculated $I-V$ characteristics presented in Fig. 2. The $I-V$ characteristic is asymmetric and non-linear. The current is symmetric for voltages up to +0.4 V and -0.4 V. As the bias increases the asymmetry

takes over and the magnitude of current increases till it reaches a peak current of -125.36 μA at -3.417 V, and 142.496 μA at 3.484 V respectively. Increasing the applied bias further on both the positive and negative bias range, the magnitude of current decreases and reaches a valley current of -45.78 μA at -5.36 V, and 51.69 μA at 5.36 V respectively-*revealing a clear* NDR *pattern*. The peaks to valley ratio (PVR) in currents are found to be 2.74 and 2.76 respectively on the negative and positive bias range. To corroborate the NDR patterns in I-V, we calculated the conductance, dI/dV, which is plotted in Fig. 2. The negative values of the conductance in the positive and negative bias range clearly confirm the two peaks. In addition, we found another small negative value for conductance at -2.91 V. Examining the I-V curve, we found from -2.8 V to -3.0 V, the current is almost constant (*blockade effect*) with a very small 0.1 μA spike at -2.88 V. Since the bias range considered in this study is quite high, we included the incoherent scattering effect (ISE) due to electron-phonon ($e-p$) coupling self consistently within Büttiker's approach [17, 24, 25] and recalculated the current at -2.88 V as well as for the bias points around it. We found the small spike of 0.1 μA at -2.88 V disappear. Inclusion of $e-p$ coupling at bias points -3.417 V and -5.36 V gives I_p and I_v as -120.17 μA and -52.21 μA with PVR of 2.30. The PVR value is found to be 2.34 for the positive bias range with the inclusion of ISE. Inclusion of ISE is found to reduce the current, but do not shift the peak or the valley position of the current. It is worthwhile to note that for the calculation of $I-V$ in which the explicit field dependent term is not included in $H(\varepsilon)$, the result do not reveal asymmetry or NDR effect, suggesting the importance of self-consistent electric field dependent screening in inducing NDR.

To understand the origin of asymmetry in current and NDR, we have calculated the bias dependent transmission function (Fig. 3) as a function of injection energy. For brevity, we have considered only five bias points. The higher current in the positive bias range (80.42 μA at 2.01 V) as compared to that for negative bias (-74.69 μA at -2.01 V) can be understood by comparing the transmission function for -2.01 V and 2.01 V. The higher transmission around $\sim 1\ eV$ for 2.01 V (within the chemical potential window) as compared to that in -2.01 V explains the higher current at the bias point 2.01 V than -2.01 V. Analysis of eigenvalues of the $H_{Mol}(\varepsilon)$, and the DOS calculated from $G(\varepsilon)$, suggest that the lowest unoccupied molecular orbital (LUMO) and LUMO+1 (Fig.4) contributes to the current at 2.01 V and -2.01 V. No change in eigenvalue spectrum of $H_{Mol}(\varepsilon)$ is found between 2.01 V and -2.01 V, suggesting the importance of channel coupling with the lead in inducing the asymmetry. Increasing the bias from 2.01 V to 3.484 V (peak position), we found a small decrease in the contribution of LUMO and LUMO+1 as the transmission peak height at $\sim 1eV$ shows a small decrease. But, as the chemical potential window increases, the highest occupied
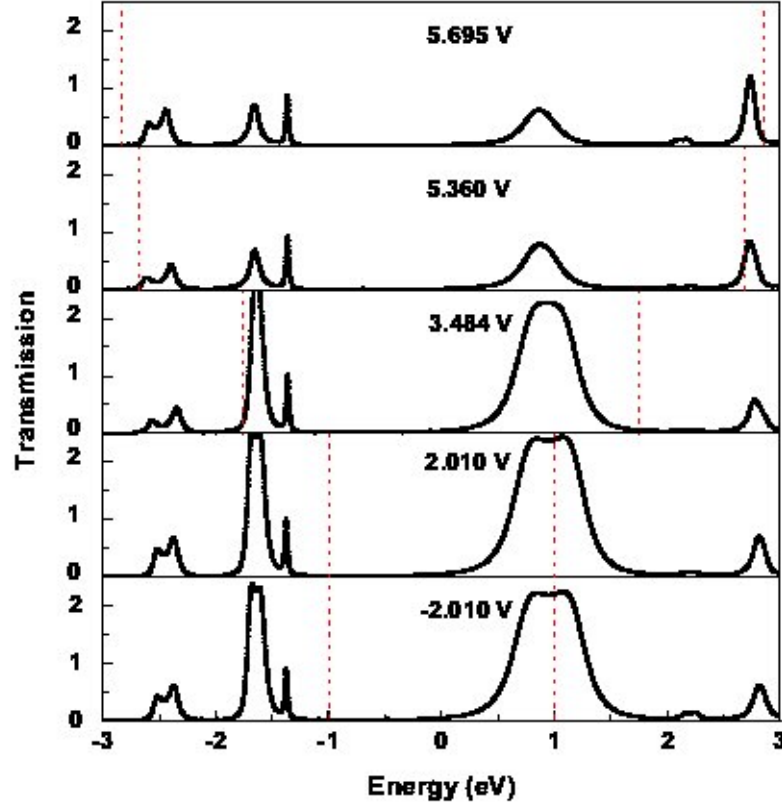
FIG. 3: Bias dependent transmission as a function of injection energy E. Fermi energy is set to zero in the energy scale; Dotted lines in each panel represents the chemical potential window.

molecular orbital (HOMO) and HOMO-1, and HOMO-2 channels (Fig. 4) contribute to the transmission at $\sim$ -1.4 eV and $\sim$ -1.6 eV, resulting to a higher net transmission and current. Increasing the bias from 3.484 V to 5.36 V (valley position), we found the contribution of LUMO and LUMO+1 to transmission decreases significantly, so also the contribution from HOMO and HOMO-1, and HOMO-2. This explains why we see less current at 5.36 V compared to that at 3.484 V, despite the contribution of additional channels HOMO-3 ($\sim$ -2.3 eV) and HOMO-4 ($\sim$ -2.5 eV) to transmission due to the increase in chemical potential window. Increasing the bias further to 5.695 V, we found the contribution of LUMO and LUMO+1 decreases by a very small amount, but the contribution of additional channels LUMO+2, LUMO+3 ($\sim$ 2.1 eV), and LUMO+4 ($\sim$ 2.8 eV) to transmission increases. Furthermore, the contribution to transmission from HOMO-3 and HOMO-4 also increases, leading to a higher net transmission and current at 5.695 V compared to that at 5.36 V. Another very interesting feature is noted from the comparison of the transmission in the three upper panels of Fig. 3. As the bias increases, the contribution to transmission from the orbital near the
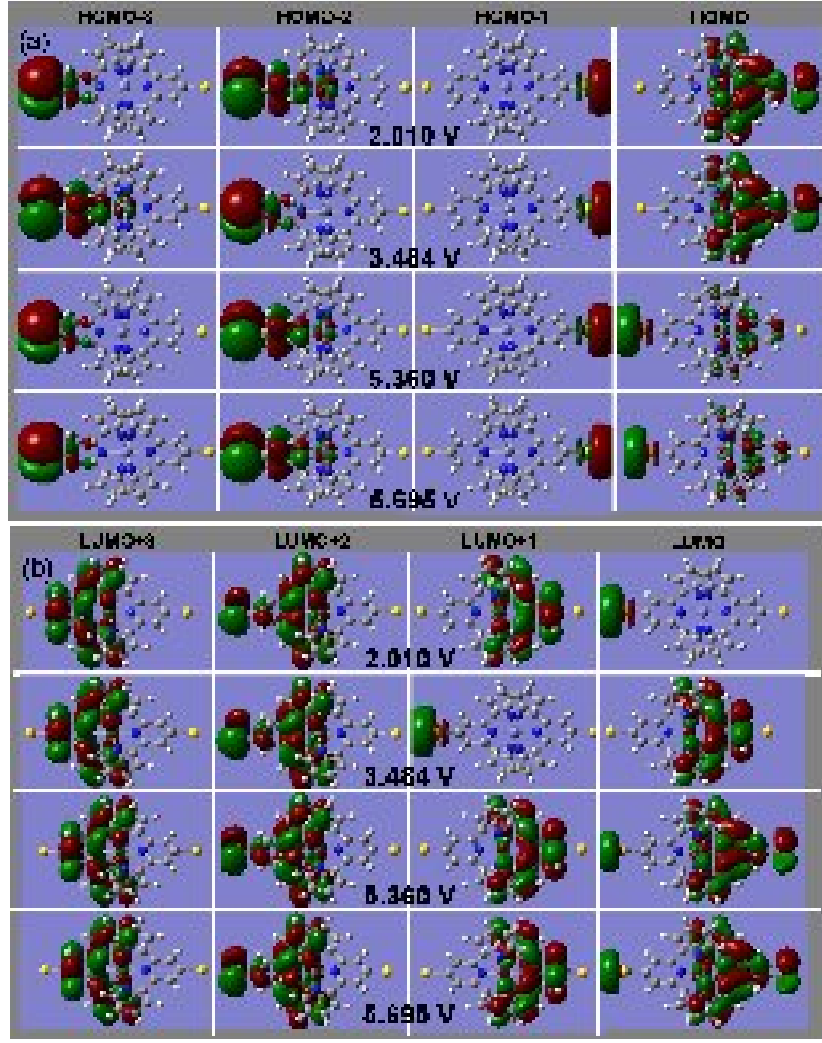
FIG. 4: (color online) (a) Occupied molecular orbital under applied bias; from right to left (column wise), the orbitals are HOMO, HOMO-1, HOMO-2, and HOMO-3. (b) Unoccupied molecular orbitals under applied bias; from right to left (column wise), the orbitals are LUMO, LUMO+1, LUMO+2, and LUMO+3. Bias changes row wise; Notation: dark gray (red) corresponds to negative lobe, and light gray (green) corresponds to the positive lobe.

Fermi energy decreases, but the contribution from the orbital away from the Fermi energy increases. This clearly suggests that the frontier orbitals and the orbitals away from the Fermi energy respond differently to the applied bias.

Thus the question arises- what is the cause for this non-monotonic feature in the net transmission which gives rise to NDR effect? Does NDR have a molecular origin or is it junction dependent? To answer these subtle questions, the eigenvalue spectrum of $H_{Mol}(\varepsilon)$ is analyzed near the Fermi energy. Though some small shift in energy levels bringing LUMO and LUMO+1 energy level closer are found with the increase of bias from 3.484 V to 5.36 V, no

shift in energy levels away from the window of chemical potential is observed, which would explain the NDR. But comparing the eigenvalue spectrum of $H_{Mol}(\varepsilon)$ and the DOS obtained from $G(\varepsilon)$, a strong bias dependent energy level broadening effect due to the coupling of the molecule with the lead is observed. Thus the question again arises- why does the broadening effect change significantly from peak to valley position? Broadening effect depends strongly on the coupling of molecular eigenstates with the lead. Thus we analyze the molecular orbital's response to the electric field (Fig.4). First, between 2.01 V and -2.01 V only a phase reversal of the molecular eigenstate is found. Second, as the bias increases (Fig.4) from 3.484 V to 5.36 V, a new phase in the broken symmetry wavefunction of the molecular [22] is emerged because of the strong mixing of the HOMO and LUMO+1 at 3.484 V to give LUMO at 5.36 V. This significant change is expected to have a strong effect on the coupling. To confirm this hypothesis, we recalculated the current at 5.36 V using coupling matrices extracted at 3.484 V. The calculated current is found to be 62.63 μA, which is higher than the original valley current. Similar calculation at 5.695 V using the bias dependent coupling matrices extracted from the self-consistent calculation at 5.360 V (valley position) gives a lower current of 50.05 μA than the original valley current, suggesting the coupling is weaker at the valley position than at 3.484 V and 5.695 V. Thus, unambiguously, we have confirmed that the non-linear coupling change arising from a bias dependent transition in broken symmetry phase of the molecular eigenstate is responsible for the NDR.

In summary, using an exhaustive first-principles approach, in which the electric field effect is explicitly included within a *many body* framework, we have identified the origin of NDR in a strongly coupled single-molecular junction. Our calculation in a FETP molecule-metal junction reveals asymmetry and strong NDR feature in the $I - V$, with high PVR of ~ 2.7 at both positive and negative bias. The origin of asymmetry in current between the positive and negative bias range is ascribed to the asymmetric channel coupling at the junction arising from the phase reversal of the molecular eigenstate. The high PVR suggests that this switching device could potentially be used as an active component in a new generation molecular electronics circuit. Most important, we found that the bias dependent transition in the broken symmetry phase of the molecular wavefunction leading to a non-linear change in the coupling between molecule and lead is the root cause for NDR. This mechanism can be used to explain NDR in other class of metal-molecule junction device.

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is determined self-consistently. The transmission for the three probe system is calculated using $T(E, V) = T_{lr} + \frac{T_{pr}T_{pl}}{T_{pr}+T_{pl}}$

as described in Ref. 21 and 24.